STUDIES IN CHLOROSULPHURIC ACID SOLVENT SYSTEM

DISSERTATION

Submitted in Partial Fulfilment of the Requirements
for the Award of the Degree of

Master of Philosophy

IN

CHEMISTRY

BY

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DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

1992

DEDICATED
TO MY
PARENTS

DIVISION OF INORGANIC CHEMISTRY
DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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CERTIFICATE

Certified that the work embodied in this dissertation entitled, "**Studies In Chlorosulphuric Acid Solvent System**" is result of original researches carried out under my supervision by **Mr. P. Shahul Hameed** and is suitable for submission for the award of M.Phil., degree of Aligarh Muslim University, Aligarh.

(MOHAMMAD SHAKIR)

ACKNOWLEDGEMENT

I would like to express my heartiest thanks to my supervisor, Dr. Mohammad Shakir, Lecturer, Department of Chemistry, AMU, Aligarh, for his appreciative guidance throughout the tenure of this research work. I also wish to thank him once again for his sustained efforts and devotion of precious time out of his busy schedule.

I am thankful to Prof. M.A. Beg, Chairman, Department of Chemistry for providing necessary research facilities.

I don't have words to express my gratitude to my parents whose constant inspiration, guidance, love and devotion helped me to complete this research work.

I wish to thank all my colleagues and my friends for their cooperation throughout this work. I am also grateful to Mr. Shoeb Iqbal Khan for providing spectral facilities at CDRI, Lucknow.

Finally I would like to extend my thanks to Mr. Ayub, for typing the manuscript of this dissertation.

P. Shahul Hameed.

(P. SHAHUL HAMEED)

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INTRODUCTION

INTRODUCTION

In nineteenth century water was considered as only solvent in which typical ionic and metathetical reaction could be carried out, the chemistry of non-aqueous solvents diverted the attention of chemists with the growing realization that reaction which could not be possible to be carried out in aqueous medium were easily performed in non-aqueous solvents. It has been found, the products from a given set of reactants can be completely changed and in some cases reaction may be reversed by change of the solvent. However, the understanding of the modes of these reaction started developing after the pioneering work of Walden and Hantzch. These workers studied the behaviour of a large number of solutes in H_2SO_4 using the cryoscopic and conductometric methods. The important discovery that carbonium ions which are strong Lewis acids can be formed and stabilized in such strong acid media encouraged the chemists to have thorough investigations in conc. H_2SO_4 and other non-aqueous strong acids as a solvent and reaction medium. Recently the strong ionizing acidic solvents like liquid HF, HSO_3F and HSO_3Cl have been found[1-10] to be a suitable fluorinating, fluorosulphonating and chlorosulphonating agent, respectively and a

variety of novel compounds of industrial importance have been synthesized by their use. The non-aqueous solvents may be classified into three major classes viz. protic, aprotic and coordinating solvents.

Protic solvent are liquid hydrogen fluoride, disulphuric acid, selenic acid and superacids, viz. SbF_5-HSO_3F, SbF_5-H_2SO_4 and SbF_5-$3SO_3$-HSO_3F. These are all strong ionizing media. Aprotic solvents are liquid sulphur dioxide, bromine trifluoride, and antimony pentafluoride whereas coordinating solvents are diemthyl formamide, methyl cyanide, acetamide, pyridine, phosphoryl chloride and dimethyl sulphoxide in which coordination takes place through the lone pair of electrons on nitrogen oxygen or sulphur atom. Chlorosulphuric acid solvent system which concerns the present work belongs to the class of protonic non-aqueous solvents. It is intermediate in strength between sulphuric acid and fluorosulphuric acid. It has been found to be very useful for the study of the mode of ionization of a variety of organic and inorganic solutes. However, recently chlorosulphuric acid solvent has been considerably exploited as a suitable medium to carry out redox reactions for the formation and stabilization of various cationic species like the carbonium ions and several polyatomic cations which under normal conditions are unstable.

Walden[11] suggested for the first time on the basis of its

specific conductance measurement that chlorosulphuric acid to be a good ionizing solvent. Robinson and Ciruna have taken the conductometric, transport and density measurement studies[12] on the solutions of alkali metal and alkaline earth metal chlorides and on their chlorosulphates in HSO_3Cl. They found that HSO_3Cl undergoes self-ionization according to the following equation :

$$HSO_3Cl \rightleftharpoons H^+ + SO_3Cl^- \qquad (1)$$

These solutes are completely ionized and act as strong electrolytes[12] according to the following general equation :

$$MCl_n + nHSO_3Cl \rightleftharpoons M^{n+} + nSO_3Cl^- + nHCl \qquad (2)$$

$$M(SO_3Cl)_n \rightleftharpoons M^{n+} + nSO_3Cl^- \qquad (3)$$

M = alkali or alkaline earth metals

n = 1 for alkali metals

n = 2 for alkaline earth metals.

Robinson and Ciruna have taken the conductivity measurement[12] on solutions of some alkyl and aryl carboxylic acids in this solvent and reported that these acids behave as simple bases and undergo protonation as shown by the following reaction:

$$RCOOH + HSO_3Cl = RCOOH_2^+ + SO_3Cl^- \qquad (4)$$

($R = CH_3$, C_6H_5)

The observed conductivity value was found to be much greater than would have been expected from normal diffusion controlled transport process. They suggested that most of the current in the solution is carried by chlorosulphate anion (SO_3Cl^-) or chlorosulphuric acidium ion ($H_2SO_3Cl^+$), the ions of self ionization which conduct by an abnormal proton transfer mechanism similar to that found for HSO_4^- and $H_3SO_4^+$ ions in sulphuric acid[13] and SO_3F^- and $H_2SO_3F^+$ ions in fluorosulphuric acid[14]. The high values of conductivity arises from a Grotthus type chains of solvent molecule.

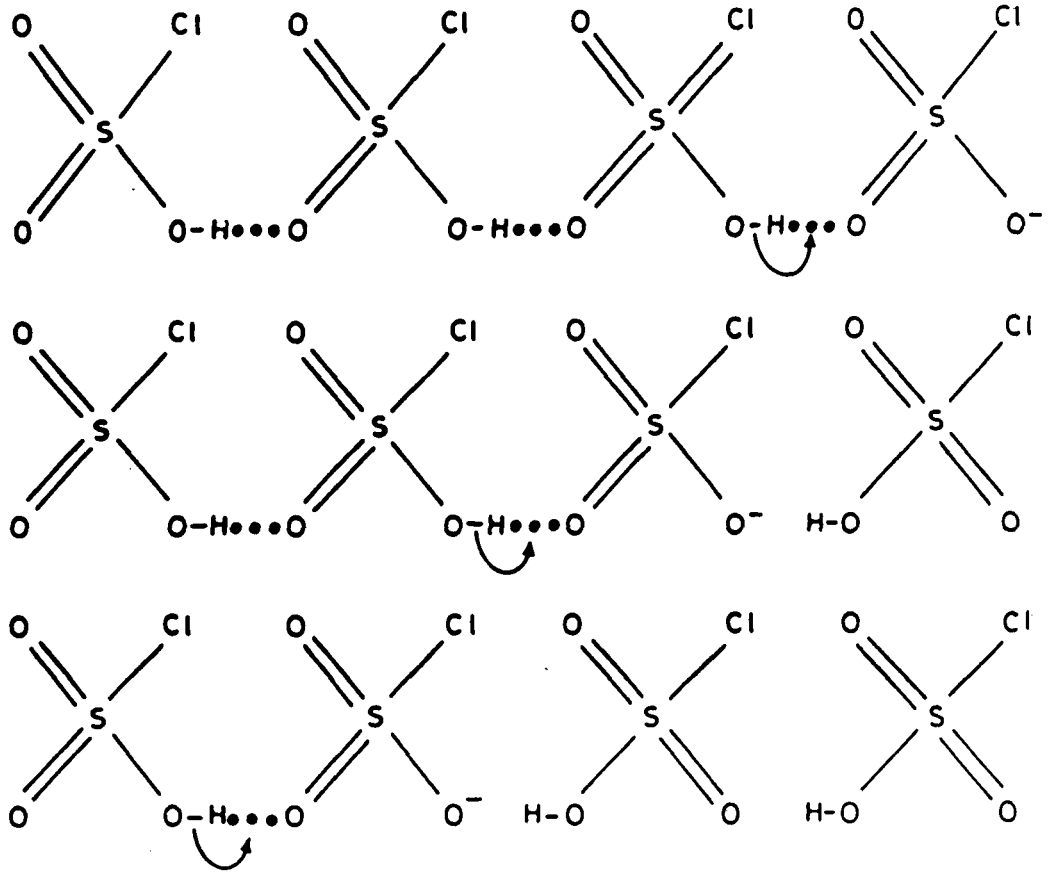


Fig. 1. Grotthus proton transport mechanism.

The low dielectric constant of HSO_3Cl (ϵ = 60) would encourage the formation of ion-pairs in solution especially for divalent metal ions of small radii, leading to a sufficient decrease in the specific conductance of the solution similar to that reported[12] for alkaline earth metal chlorosulphates in chlorosulphuric acid solution.

It has been reported[15] from the results of electrical conductivity measurements and Raman spectra of solutions in HSO_3Cl that $SeCl_4$ and $TeCl_4$ ionize quantitatively in this solvent system producing $SeCl_3^+$ and $TeCl_3^+$ cations according to the following reaction :

$$MCl_4 + HSO_3Cl = MCl_3^+ + SO_3Cl^- + HCl \qquad (5)$$

M = Se, Te

A large number of inorganic solutes have been proved to behave as bases in HSO_3Cl solvent. The mode of ionization and the formation of the cationic species resulted from these solutes have been reported from this laboratory as given below:

It has been found[16] that in HSO_3Cl phosphorous pentoxide gives protonated phosphoric acid, and phosphoryl chloride was incompletely protonated according to the reactions given below :

$$P_2O_5 + 11HSO_3Cl = 2H_4PO_4^+ + 4S_2O_2Cl_2 + H_2SO_4 + HCl + 2SO_3Cl^- \qquad (6)$$

$$POCl_3 + HSO_3Cl = POHCl_3^+ + SO_3Cl^- \qquad (7)$$

The partial protonation of $POCl_3$ have also been confirmed by ^{31}P-n.m.r. spectroscopic studies conducted by Waddington and coworkers[17].

It has been shown[18] that ionization of organic acid anhydrides in HSO_3Cl produces acidium ion, ($RCO_2H_2^+$) rather than the acylium ion, (RCO^+) similar to that reported in other solvent systems, i.e.

$$(RCO)_2O + 4HSO_3Cl = 2RCO_2H_2^+ + S_2O_5Cl_2 + 2SO_3Cl^- \qquad (8)$$

(R = CH_3 or C_6H_5)

Conductivity of these colourless solution having γ value of 2.00 is consistent with above mode of ionization. The NMR spectra of their solutions in HSO_3Cl contained only 1 peak shifted to lowerfield assigned to the methyl or phenyl protons of the acidium ion. However, the dicarboxyclic acid anhydrides have been found[18] to act as weak bases in HSO_3Cl giving the corresponding intramolecularly hydrogen bonded protonated anhydrides.

Recently it has been shown[19-21] that HSO_3Cl itself act as oxidizing agent which oxidize the elements S, Se and Te producing polyatomic cationic species S_4^{2+}, S_{16}^{2+}, Se_4^{2+} and

Te_4^{2+} containing the elements in low oxidation state. Some of these cationic species have been found to have sufficient life-time in solution. The conductometric redox-titration in HSO_3Cl by using suitable oxidizing agents viz. $K_2S_2O_8$, SeO_2 and TeO_2 indicated that a few of the above mentioned polyatomic cationic species can be further oxidized to +1 or +4 oxidation states depending on concentrations of the appropriate oxidizing agents in the solution.

Iodine and some of its compounds viz. KI, ICl, HIO_3 and I_2O_5 ionize in HSO_3Cl producing a stable cationic species I_3^+ in solution according to the following reactions :

$$3I_2 + 4HSO_3Cl = 2I_3^+ + SO_2 + 2HCl + 2SO_3Cl^- + H_2SO_4 \qquad (9)$$

$$5I_2 + 4HSO_3Cl = 2I_5^+ + SO_2 + 2HCl + 2SO_3Cl^- + H_2SO_4$$

$$I_5^+ \rightleftharpoons I_3^+ + I_2 \qquad (10)$$

$$HIO_3 + 2HSO_3Cl = IO_2SO_3Cl + H_2SO_4 + HCl$$

$$4IO_2SO_3Cl = I_3^+ + I(SO_3Cl)_3 + SO_3Cl^- + 4O_2 \qquad (11)$$

$$I_2O_5 + 2HSO_3Cl = 2HIO_3 + S_2O_5Cl_2$$

$$HIO_3 + 2HSO_3Cl = IO_2SO_3Cl + H_2SO_4 + HCl$$

$$4IO_2SO_3Cl = I_3^+ + I(SO_3Cl)_3 + SO_3Cl^- + 4O_2 \qquad (12)$$

$$3KI + 8HSO_3Cl = I_3^+ + 2SO_2 + 3K^+ + 2H_2SO_4 + 4HCl + 4SO_3Cl^- \qquad (13)$$

$$4ICl + 4HSO_3Cl = I_3^+ + 4HCl + I(SO_3Cl)_3 + SO_3Cl^- \quad (14)$$

The behaviour of hydrazine sulphate, phenyl hydrazine and a few substituted phenyl hydrazines in HSO_3Cl has been investigated[22] conductometrically with a view to determining their relative basicities with regard to the formation of a diprotonated species. It has been found that phenyl hydrazine and 1-naphthyl hydrazine undergo complete protonation, according to the following general reaction :

$$R\text{-}NH\text{-}NH_2 + 2HSO_3Cl = R\text{-}\overset{+}{N}H_2\text{-}\overset{+}{N}H_3 + 2SO_3Cl^- \quad (15)$$

(R = C_6H_5 or $C_{10}H_7$)

While hydrazine sulphate undergoes incomplete ionization to produce a dicationic species as shown below :

$$NH_2\text{-}NH_2.H_2SO_4 + 2HSO_3Cl = \overset{+}{N}H_3 - \overset{+}{N}H_3.H_2SO_4 + 2SO_3Cl^- \quad (16)$$

The extent of protonation in 2,4-dinitrophenyl hydrazine and 2,5-dichlorophenyl hydrazine is lower as compared to that in phenyl hydrazine and only monoprotonation has been indicated in these case.

Ionization of some inorganic solutes such as phosphorous trichloride, tribromide, pentachloride, pentabromide and hexachloroiodide in HSO_3Cl has been investigated conductometrically[23]. It has been reported that pentahalides and hexa-

chloroiodide ionize producing the stable cationic species PX_4^+ according to the following reaction :

$$PX_5 + HSO_3Cl = PX_4^+ + SO_3Cl^- + HX \quad (17)$$

(X = Cl, Br)

$$2PCl_6I + 3HSO_3Cl = 2PCl_4^+ + 2SO_3Cl^- + I_2 + SO_3 + 3HCl + Cl_2 \quad (18)$$

Whereas trihalides are oxidised producing ultimately the conjugate acid POH^+X_3 in this solvent

$$PX_3 + 2HSO_3Cl = POH^+X_3 + SO_2 + HCl + SO_3Cl^- \quad (19)$$

The conductometric redox-titrations of phosphorus trihalides with the appropriate halogens and interhalogen (ICl) compounds exhibit a sharp break at mole ratios $PCl_3/Br_2 = 1.00$ and $PBr_3/ICl = 3.0$ indicating the formation of cationic species PCl_3Br^+ and PBr_3Cl^+ as stable entities in solutions. The mode of reaction can be expressed by the following equations :

$$PCl_3 + Br_2 + HSO_3Cl = PCl_3Br^+ + HBr + SO_3Cl^- \quad (20)$$

$$PBr_3 + ICl + 7HSO_3Cl = 3SO_3Cl^- + 3PBr_3Cl^+ + HI + SO_2 + 2H_2SO_4 + 2HCl \quad (21)$$

It has been observed that the species PCl_3I^+ and PBr_3I^+ do not exist as stable entities in the solution which may be due to the greater solvation energy required for the stabili-

zation of these cations because of their bulky sizes[24].

However, the solutes like $AsCl_3$, SbF_3 and $SbCl_3$ are only partially ionized, producing the cationic species MX_2^+ in the solution. The basic ionization constants (Kb) of these solutes have also been evaluated[25]. Whereas $SbCl_4$, $BiCl_3$ and VCl_3 remain insoluble in this solvent.

The behaviour of a few organo tellurium (IV) derivatives has also been studied[26] in HSO_3Cl with a view to examining the mode and extent of their ionization and the possible formation and stabilization of novel types of cationic species formed in the solution. Conductometric measurements on solutions of α-$(CH_3)_2TeI_2$, α-$(C_2H_5)_2TeI_2$ and $(C_6H_5)_2TeCl_2$ in HSO_3Cl indicate that both of the tellurium-halogen bonds are cleaved resulting in the formation of solvolysed species, $R_2Te(SO_3Cl)_2$, [R = CH_3, C_2H_5, C_6H_5] which further ionize giving a dicationic species $[R_2Te]^{2+}$ remaining as stable entity in the solution as represented below :

$$R_2Te(SO_3Cl) \longrightarrow R_2Te^{2+} + 2SO_3Cl^- \qquad (22)$$

[R = CH_3, C_2H_5, C_6H_5]

Formation of interhalogen cations IX_2^+ and I_2X^+ (X = Cl, Br) in strong ionizing non-aqueous acidic media has been the subject of considerable interest during the last one or two

decades[27,28]. Recently the formation of interhalogen cation, IBr_2^+ as a stable entity has been reported[29] from this laboratory by utilizing the oxidation of I_2, KI and HIO_3 involving Br_2 as an oxidizing agent in HSO_3Cl which has been confirmed on the basis of conductometric and spectroscopic studies. The possible mode of ionization may be written as follows :

$$I_2 + 2Br_2 + 4HSO_3Cl = 2IBr_2^+ + 2SO_3Cl^- + SO_2 + H_2SO_4 + 2HCl \quad (23)$$

$$KI + Br_2 + 4HSO_3Cl = K^+ + IBr_2^+ + 2SO_3Cl^- + SO_2 + H_2SO_4 + 2HCl \quad (24)$$

$$HIO_3 + Br_2 + 2HSO_3Cl = IBr_2^+ + SO_3Cl^- + H_2SO_4 + HCl + O_2 \quad (25)$$

This cation is also generated in the solution mixture $Br_2/(2I_2 + HIO_3)$ in HSO_3Cl at the mole ratio $Br_2/(2I_2 + HIO_3)$ = 5.0 as shown below :

$$2I_2 + HIO_3 + 5Br_2 + 8HSO_3Cl = 5IBr_2^+ + 8SO_3Cl^- + 3H_3O^+ \quad (26)$$

It has been reported[30] from this laboratory that the quinqivalent vanadium compounds e.g. V_2O_5, $VOCl_3$ and MVO_3 [M = Na, NH_4] act as weak electrolytes in chlorosulphuric acid giving a similar solvolysed species $H[VO(SO_3Cl)_4]$ according to the following reactions :

$$V_2O_5 + 11HSO_3Cl = 2H[VO(SO_3Cl)_4] + 3H_2SO_4 + 3HCl \quad (27)$$

$$VOCl_3 + 4HSO_3Cl = H[VO(SO_3Cl)_4] + 3HCl \quad (28)$$

$$MVO_3 + 7HSO_3Cl = H[VO(SO_3Cl)_4] + 2H_2SO_4 + M^+ + SO_3Cl^- + 2HCl \quad (29)$$

$$H[VO(SO_3Cl)_4] + HSO_3Cl \rightleftharpoons H_2SO_3Cl^+ + [VO(SO_3Cl)_4]^- \quad (30)$$

The observed autoprotolysis constant K_{ap} of this solvent is $4.59 \pm 0.20 \times 10^{-6}$ Moles^2 Kg^{-2} which is smaller to that reported[31,32] for 100% H_2SO_4 suggesting that autoionization of the solvent is completely repressed even in dilute solutions of the electrolytes.

The solvolytic reactions of chromyl chloride and chromium trioxide[33,34] with excess of HSO_3Cl used as a medium as well as the chlorosulphonating agent yield a moss-green amorphous solid at room temperature whereas a brown coloured crystalline solid is formed at 60°C according to the following reactions

$$CrO_2Cl_2 + 2HSO_3Cl = CrO_2(SO_3Cl)_2 + 2HCl \quad (31)$$

$$CrO_3 + 3HSO_3Cl = CrO_2(SO_3Cl)_2 + H_2SO_4 + HCl \quad (32)$$

The resultant compounds have been shown to be chemically the same, characterized as $CrO_2(SO_3Cl)_2$ i.e. [dioxobis(chlorosulphato)Cr(VI)] based on physico-chemical studies having the structure as shown in Figure-2.

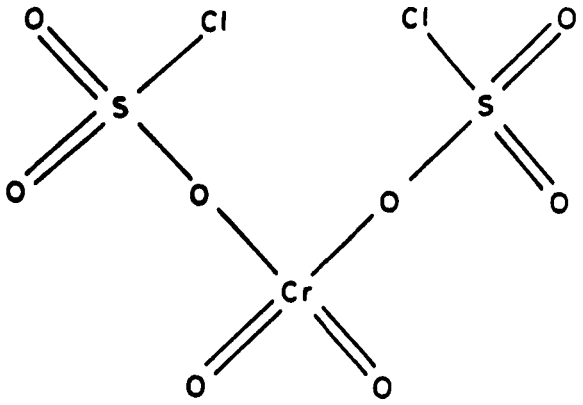


Fig.2

A similar type of compound was obtained[33] by the reaction of the oxo-anions, CrO_4^{2-} and $Cr_2O_7^{2-}$ with HSO_3Cl according to the following reactions :

$$K_2CrO_4 + 6HSO_3Cl = 2K^+ + CrO_2(SO_3Cl)_2 + 2SO_3Cl^- + 2H_2SO_4 + 2HCl \quad (33)$$

$$K_2Cr_2O_7 + 9HSO_3Cl = 2K^+ + 2CrO_2(SO_3Cl)_2 + 3HCl + 3H_2SO_4 + 2SO_3Cl^- \quad (34)$$

It has been systematically observed[35] that the solutions of a few Pb(II) compounds e.g. $Pb(CH_3COO)_2$ and $PbCl_2$ in chloro-sulphuric acid produced a yellow coloured solution of $Pb(SO_3Cl)_2$ as shown by the reactions given below :

$$Pb(CH_3CO_2)_2 + 4HSO_3Cl = Pb(SO_3Cl)_2 + 2CH_3CO_2H_2^+ + 2SO_3Cl^- \quad (35)$$

$$PbCl_2 + 2HSO_3Cl = Pb(SO_3Cl)_2 + 2HCl \quad (36)$$

There have been a variety of reports on chlorosulphonating behaviour of chlorosulphuric acid and a variety of metal chlorosulphates[36-38], $M(SO_3Cl)_2$ [M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg] and $M(SO_3Cl)_3$[39] [M = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Td, Dy] have been synthesized by carrying out solvolytic reactions on corresponding metal acetates and benzoates, respectively where HSO_3Cl acts both as medium of reaction as well as chlorosulphonating agent. A number of the complexes of the types $ML_2(SO_3Cl)_2$, $ML_4(SO_3Cl)_2$ and $ML_3(SO_3Cl)_3$[40] [M = Transition metals, or rare earth metals, L = Pyridine N-oxide, triphenylphosphine, methyl cyanide, 2,2'-bipyridine, pyridine and acridine have also been prepared and characterized with a view to examining their stereochemistry and extent of coordination of SO_3Cl^- anion to the complex cations, $[ML_n]^{m+}$ (n = 2, 4 for m = 2, n = 3 for m = 3). The mode of bonding of SO_3Cl^- in these metal chlorosulphates as well as their complexes has been confirmed by comparing the i.r. spectra of these compounds with that of the free SO_3Cl^- group. The positive shift in the sym. SO_3 stretch $\nu_1(A)$ and splitting of the doubly degenerate (E) modes suggest a considerable cation-anion interaction. This cation-anion interaction lowers the symmetry of chlorosulphate group, SO_3Cl^- from C_{3v} (as exists in $CsSO_3Cl$)[8] to a reduced C_s. The observed low conductivity values of these compounds further confirm that the chlorosulphate group is covalently bonded to the metal ions and complex cations in metal chlorosul-

phates and their complexes, respectively. The overall geometry of these compounds has been inferred from the band positions in the electronic spectra and the observed values of magnetic moment.

A few organo tellurium derivatives $R_2Te(SO_3Cl)_2$ ($R = CH_3$, C_2H_5) have also been synthesized[41] utilizing the metathetical reaction on corresponding iodides with HSO_3Cl.

$$R_2TeI_2 + 2HSO_3Cl = R_2Te(SO_3Cl)_2 + 2HI \qquad (37)$$

($R = CH_3$, C_2H_5)

These compounds have been characterized on the basis of i.r., u.v. and ^1H-NMR spectral studies.

It has been shown[42] that both sodium selenite Na_2SeO_3 and sodium tellurite Na_2TeO_3 dissolve in chlorosulphuric acid yielding highly conducting yellow coloured solutions. Conductometric and spectrophotometric studies on these solutions reveal that these yellow coloured solutions contain the solvolysed species, $MO(SO_3Cl)_2$ (M = Se or Te). The observed average γ-values of sodium selenite and sodium tellurite have been found to be about 1.65 and 1.50, respectively which is consistent with the following possible modes of ionization.

$$Na_2MO_3 + 6HSO_3Cl = 2Na + MO(SO_3Cl)_2 + 2HCl + 2H_2SO_4 + 2SO_3Cl^- \qquad (38)$$

(M = Se, Te)

The complexes sodium hexakis(chlorosulphato) iridate, $Na_2Ir(SO_3Cl)_6$ and sodium tetrakis(chlorosulphato) palladate, $Na_2Pd(SO_3Cl)_4$ were synthesized[43] by carrying out the solvolytic reaction of the corresponding solid sodium hexachloroiridate and sodium tetrachloropalladate with HSO_3Cl, according to the following equations (39 and 40) which were identified by elemental analyses as well as by spectroscopic techniques.

$$Na_2IrCl_6 + 6HSO_3Cl \longrightarrow Na_2Ir(SO_3Cl)_6 + 6HCl \qquad (39)$$

$$Na_2PdCl_4 + 4HSO_3Cl \longrightarrow Na_2Pd(SO_3Cl)_4 + 4HCl \qquad (40)$$

A number of mixed metal chlorosulphates have also been synthesized[44] by carrying out the solvolytic reaction of $M_2[HgI_4]$[(M = K, Cu(I)] with HSO_3Cl resulting in the formation of colourless solid compounds of the type $M_2[Hg(SO_3Cl)_4]$ according to the following reaction :

$$M_2HgI_4 + 4HSO_3Cl \longrightarrow M_2[Hg(SO_3Cl)_4] + 4HI \qquad (41)$$

[M = K, Cu(I)]

However, the compounds with general formula $K_2[Hg(SO_3Cl)_n I_{4-n}]$ as (n = 1, 2 and 3) have also been prepared by the reaction of $KHgI_4$ with frozen HSO_3Cl in 1:3, 1:2 and 1:1 molar ratios. All these compounds have been characterized by various physico-chemical studies.

In view of the work described above it is clear that HSO_3Cl can acts as a suitable solvent for the study of mode of ionization of different types of organic and inorganic solutes as well as a suitable chlorosulphonating agent for the synthesis of the various metal chlorosulphates and mixed metal chlorosulphates.

The following physical properties of HSO_3Cl solvent reflect its importance as non-aqueous solvent.

Boiling point[45,46]	62°C at 2.7 mm
	78°C at 21.5 mm
	152°C at 760 mm
Melting point[45]	-80°C
Density[47]	1.741 gm/c.c.
Viscosity[48]	0.0243 P at 14°C
Dielectric constant[49]	60 ± 10 at 14°C
Molar susceptibility[47]	46.60
Specific heat[50]	0.282 cal/gm.
Specific conductance[12]	4.0×10^{-4} ohm^{-1} cm^{-1}
Hammett Acidity Value[51]	-13.80

PRESENT WORK

PRESENT WORK

There have been a quite number of reports that HSO_3Cl acts both as medium of reaction and chlorosulphonating agent. In view of above facts a variety of metal bis(chlorosulphates)[36-38], $M(SO_3Cl)_2$ [M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg], tris(chlorosulphates), $M(SO_3Cl)_3$[39,40] [M = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Td, Dy] and oxychlorosulphates[33,34] have been prepared and characterized. The coordinating ability of SO_3Cl^- group has been demonstrated by the synthesis of a number of the complexes with well known strong donar bases with pyridine, 2,2'-bipyridine, acridine, pyridine N-oxide and methyl cyanide. A few mixed metal chlorosulphates of the types $M[M'(SO_3Cl)_3]$[52-54] [M = alkali or alkaline earth metals, M' = B, Al, Ga]; $M_2[Hg(SO_3Cl)_4]$[44] [M = K, Cu, Et_4N]; $K_2[Hg(SO_3Cl)I_{4-n}]$ (n = 1,2 3) and $Na_2[M(SO_3Cl)_n]$[43] [M = Pd, or Ir for n = 4 and 6, respectively] have also been prepared from this laboratory by carrying out solvolytic reactions, on the corresponding complex anions. The evidence regarding the structure and bonding in these compounds have been deduced from the number and energies of bands characteristic of anion vibrations in the i.r. spectra. The spectra of the ionic chlorosulphates $Me_4\overset{+}{N}SO_3Cl^-$ and $PCl_4^+SO_3Cl^-$ were explained by Waddington and Klanberg[55] by comparison with those reported[56] for the corresponding fluoro-

sulphates. The number of multiplet bands observed in the 530 to 650 cm^{-1} region of the i.r. spectrum of $NaSO_3Cl$ were assigned[57] by steger ciurea in terms of removal of degeneracy of the asymmetric bending vibrations and a Fermi-resonance interaction between the symmetric SO_3 bending and a combination band of the S-Cl stretching and S-Cl wagging vibrations of the chlorosulphate group. However, a detailed analyses of the i.r. spectra of ionic chlorosulphates was first presented by Robinson and Ciruna[8] on the basis of a C_{3v} symmetry, of the free chlorosulphate ion. The free chlorosulphate ion, as is expected to exist in $CsSO_3Cl$, exhibits six fundamental mode of vibrations with three doubly degenerate modes viz. sym. SO_3 Str. $\nu_1(A)$ and asym. SO_3 Str. $\nu_4(E)$, sym. SO_3 def. $\nu_3(A)$ and asym. SO_3 def. $\nu_5(E)$, S-Cl str. $\nu_2(A)$ and S-Cl wag. $\nu_6(E)$. The degenerate modes would split resulting in up to nine fundamentals due to symmetry lowering of the chlorosulphate ion to a reduced C_s symmetry, if any appreciable covalent bonding occurs between SO_3Cl^- anion and the metal ion.

In the view of synthetic utility of SO_3Cl^- anion as well as the use of HSO_3Cl as medium of reaction. It was, therefore, thought worthwhile to synthesize a few transition metal mono (chlorosulphates), $M(SO_3Cl)$ [M = Hg(I), Ag(I)] and tri(chlorosulphates), $M(SO_3Cl)_3$ [M = Cr, Mn, Fe] and their complexes with

strong donar organic bases, namely acetonitrile, pyridine, pyridine N-oxide, 2,2'-bipyridine, acridine and triphenylphosphine with a view to examining their sterochemistry and the mode of coordination of the anion to the metal ions as well as the complex cations.

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

Various physico-chemical methods have been employed to confirm the bonding and structure of newly synthesized compounds viz. :

1. Infra-red spectroscopy
2. Ultra-violet and visible (ligand-fields) spectroscopy
3. Magnetic susceptibility measurements
4. Molar conductance measurements.

A brief description of these methods have been discussed below :

The results of elemental analyses for C, H, N were obtained from the micro-analytical laboratory of the CDRI Lucknow. The chlorine and sulphur estimation were done gravimetrically and the metals were estimated by titrating with standard EDTA solution.

The IR and far IR spectra were recorded as nujol mulls, in the polyethylene envelopes sealed from all sides using PYE Unicam SP3 - 300 (4000-200 cm^{-1}) spectrophotometer in the chemistry department of G.N.D. University, Amritsar.

Savoie and Giguere[58] have taken the IR spectra of HSO_3Cl for the first time in all three states upto $60^{o}C$. Chackalackal

and coworkers[59] have assigned the frequencies observed in the i.r. spectra of the monomer as the characteristic SO_2 rocking, S-Cl stretching, S-O-H stretching, SO_2 symmetric stretching, SO_2 asymmetric stretching and OH stretching vibrations. Later it was mentioned[8] that the SO_3Cl^- ion which has a C_{3v} symmetry is expected to show six modes of vibration as a symmetric SO_3 stretching $\nu_1(A)$ and asymmetric SO_3 stretching $\nu_4(E)$, a symmetric SO_3 bending $\nu_3(A)$ and asymmetric SO_3 bending $\nu_5(E)$, a S-Cl stretching $\nu_2(A)$ and S-Cl wagging $\nu_6(E)$. It has been confirmed from the study of few alkali and alkaline earth metal chlorosulphates[8] that the positions of these bands are not much altered except that the symmetric SO_3 stretch. $\nu_1(A)$ vibration undergoes a positive shift if there is an increased interaction between metal ion and SO_3Cl^- group.

The frequency observed in the IR spectra of different organic molecules are given below :

CH_3CN - The methyl cyanide molecule which belongs to the point group C_{3v} shows eight normal modes of vibrations[60] of which four belong to the degenerate (E)modes. It has been indicated that this molecule can coordinate through nitrogen[61-66] as well as via the triple bond[67]. The position of the characteristic vibrations are affected when methyl cyanide undergoes coordination to the metal ions. However, the nitrile frequency (C≡N,

2255 cm^{-1}) shifts towards higher wave numbers (~ 35 cm^{-1}) if CH_3CN coordinates through the nitrogen atom.

PYRIDINE : The pyridine may coordinate through the nitrogen atom which may be inferred from the positive shift in the three characteristic ring vibrations, i.e. 16b (out-of-plane ring deformation), 6a and 8a (in-plane-ring deformations) as compared to free pyridine molecule[68], where three vibrations have been reported to appear at 403, 601 and 1578 cm^{-1}, respectively.

2,2'-BIPYRIDINE : 2,2'-Bipyridine exhibits three important ring vibrations viz. the out-of-plane ring deformation, 16b and in-plane ring deformation, 6a and 8a occurs at 402, 619 and 1590 cm^{-1}, respectively[69]. It has been found that the two lower wave number bands are very sensitive and undergo positive shift after complexation.

ACRIDINE : The two strong bands appeared at 1515 and 1555 cm^{-1} in the i.r. spectrum of the free acridine corresponding to ν C=C and νC=N stretching vibrations, respectively[70]. The positive shift of about 75 cm^{-1} and 100 cm^{-1} has been observed for the ν C=C and νC=N vibrations, respectively after complexation of acridine to metal ions indicating the coordination through the N-atom[70,71].

TRIPHENYLPHOSPHINE : The triphenylphosphine moiety shows strong bands in 500 - 1480 cm^{-1} region. The two strong bands, one at 742 cm^{-1} and another at 695 cm^{-1} are characteristic of a monosubstituted benzene ring[72]. However, bands in the region 1092 - 1118 cm^{-1} may resonably be assigned to νP-C modes[73]. A strong band at ca 500 cm^{-1} is a diagonestic feature of the triphenylphosphine. The strong bands at 1430 - 1480 cm^{-1} are associated to benzene ring. The coordination of triphenylphosphine may be inferred by positive shift in νP-C mode and appearance of a new band at ca 270 cm^{-1} assignable to νM-P[74].

PYRIDINE N-OXIDE : It shows strong absorption at 1243 cm^{-1} characteristic of the νN-O stretching frequency. The observed negative shift ($\sim$ 25 cm^{-1}) in νN-O mode in pyridine N-oxide complexes indicates its coordination through oxygen atom[75,76].

M-O STRETCHING VIBRATION : The medium intensity band observed in the 360 - 390 cm^{-1} region may reasonably be assigned as νM-O stretching vibration[36].

M-N STRETCHING VIBRATION : The M-N stretching frequency provides direct information regarding coordination. It appears in the low frequency region and depends on the following factors:

1. Mass of the metal and ligand,

2. Oxidation number of metal ion,
3. Coordination of metal ion,
4. Geometry of complex,
5. Basicity of ligand molecule,
6. Bridging or non-bridging anions and
7. Ligand field stabilizing energy.

Electronic spectra have been recorded in DMSO by using a PYE Unicam 8800 spectrophotometer at room temperature.

Results of magnetic susceptibility measurements have been obtained by using Faraday balance at 25°C, in the chemistry department of G.N.D. University, Amritsar.

The electrical conductivity measurement is one of the simplest and easily available technique, used for characterization of compounds. It gives direct information regarding whether a given compound is ionic or covalent. For this purpose the measurement of molar conductance (Λ_m) which is related to the conductance value in the following manner :

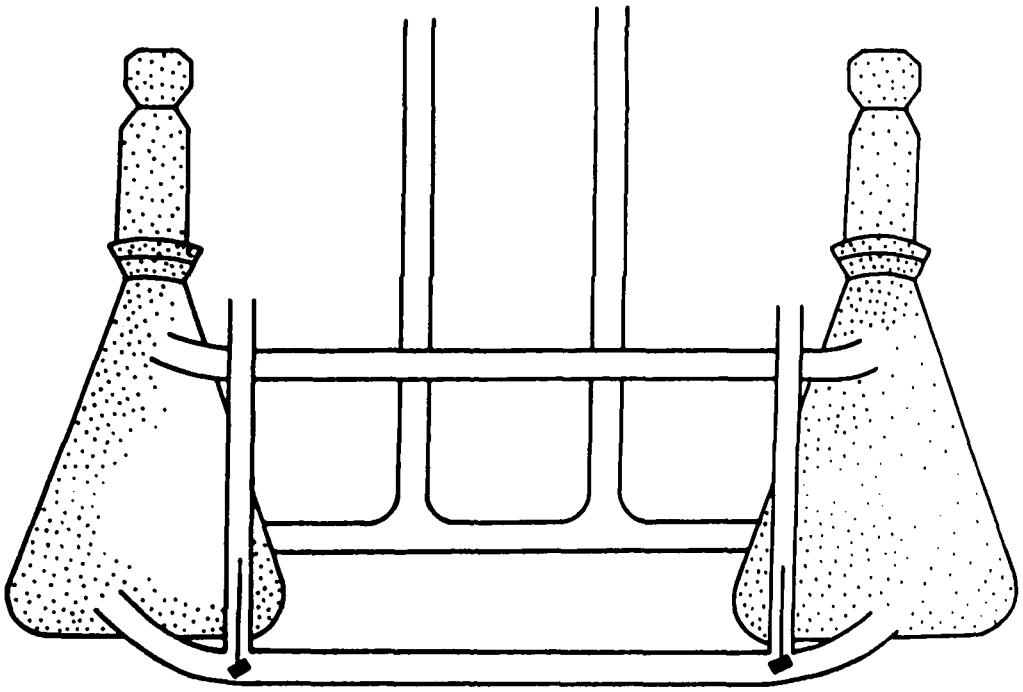
$$\Lambda_m = \frac{\text{Cell constant X conductance}}{\text{Concentration of solute expressed in moles } cm^{-3}}$$

The solution of $10^{-3}M$ strength were used for the conductance measurement.

Molar conductance values of different types of electrolytes in few solvents are given below.

A 1:1 electrolyte may have a value of 75 - 95 Ohm^{-1} Cm^2 $mole^{-1}$ in CH_3NO_2, 50 - 75 Ohm^{-1} Cm^2 $mole^{-1}$ in DMSO, 72 - 90 Ohm^{-1} Cm^2 $mole^{-1}$ in DMF and 100 - 160 Ohm^{-1} Cm^2 $mole^{-1}$ in CH_3CN[65,77,78]. Similarly a solution of 2:1 electrolyte may have value of 150 - 180 Ohm^{-1} Cm^2 $mole^{-1}$ in CH_3NO_2, 130 - 170 Ohm^{-1} Cm^2 $mole^{-1}$ in DMF and 140 - 220 Ohm^{-1} Cm^2 $mole^{-1}$ in CH_3CN[65,77,78].

The cell used in the present work is the same as designed by Solomons[79] as shown in the figure (3). It consists of 10 cm long tube containing the electrodes joined with two 100 ml conical flasks. The electrodes made from platinum foil (1 cm^2) and were firmly fixed on the tube so that no displacement could occur. The conical flasks were fitted with socket (B-14 standard joint) and were capped (B-14 standard joint) to exclude all moisture from the cell.



CONDUCTIVITY CELL

FIG. 3

EXPERIMENTAL

EXPERIMENTAL

Pure chlorosulphuric acid (Riedel), Mercurous chloride and silver acetate (Aldrich) were commercially available and used as such.

The manganese(II)acetate dihydrate and potassium permanganate were commercially pure samples and used after recrystallization. The compound manganese(III)acetate dihydrate was synthesized according to the reported method[80] and was used after dehydration. While anhydrous chromium(III) chloride and iron(III) chloride (Aldrich) were used as such.

The ligands acridine, 2,2'-bipyridine, triphenylphosphine, pyridine N-oxide (all BDH) were commercially pure samples, and were used as received. Methyl cyanide (BDH) and pyridine (E. Merck) were used after drying over calcium hydride followed by distillation.

The solvent glacial acetic acid was used as such while thionyl chloride, dimethyl sulphoxide and diethyl ether were distilled and dried before use.

Preparation of Metal mono(chlorosulphates), $M(SO_3Cl)$ [M = Hg(1), Ag(2)] :

An anhydrous mercurous chloride and silver acetate (~5 gm)

were slowly added to an excess of chlorosulphuric acid taken in a closed reaction vessel and the temperature of the reaction mixtures were maintained below 40°C by cooling in an ice-bath as an exothermic reaction took place. When the reaction was completed the solutions were magnetically stirred for about 6 hours. The colourless solid mass thus formed was separated through a filteration frit washed several times with HSO_3Cl and $SOCl_2$ and dried under vacuum at 60-80°C to a constant weight.

Preparation of Manganese(III)acetate, $Mn(CH_3COO)_3.2H_2O$:

19.6 g (80 m.moles) of $Mn(CH_3COO)_2.2H_2O$ powder was added to 200 ml of glacial acetic acid at the boiling temperature and was stirred until completely dissolved. Then $KMnO_4$ powder (3.1 g, 20 m.mol) was gradually added and the mixture heated for a short time with constant mechanical stirring. After cooling, 3 ml of water was added to the dark brown solution. The mixture was allowed to stand overnight. The formation of crystallization nuclei was promoted by frequent rubbing of the container walls with a glass rod. The solution was allowed to stand for a few more days with frequent stirring until the mother liquor was almost colourless. The solid compound thus formed then filtered off with suction, washed with some glacial acetic acid and recrystallized giving the cinnamon brown crystals of a silky luster.

Preparation of Metal tris(chlorosulphates), $M(SO_3Cl)_3$ [M = Cr(3), Mn(4),Fe(5)] :

An anhydrous chromium(III) chloride, manganese(III) acetate and iron(III)chloride (5 gm) were slowly added in excess of chlorosulphuric acid (40 ml) in closed reaction vessel. A vigrous exothermic reaction took place. The reaction vessel was put into an ice-bath to control the temperature upto 40°C. After the completion of the reaction, mixture was magnetically stirred for 8 hrs. affording the isolation of solid products which were filtered through Schlenk filteration frit, washed several times with chlorosulphuric acid and lastly with thionyl chloride and dried in vacuum at 60-80°C to a constant weight.

Synthesis of pyridine, pyridine N-oxide, acridine, triphenylphosphine and 2,2'bipyridine complexes of metal mono(chlorosulphates) :

These complexes were prepared by reacting methyl cyanide solution of the appropriate metal chlorosulphates with an excess of ligand. A detailed procedure of the preparation is given as follow :

Synthesis of tris(triphenylphosphine) metal (I) chlorosulphates, $[M(Ph_3P)_3SO_3Cl]$ [M = Hg(6), Ag(7)] :

0.04 mole metal chlorosulphates dissolved in methyl cyanide (~25 ml), was taken in a closed reaction vessel and an excess (0.12 mole) of hot triphenylphosphine solution in methyl cyanide was added. The crystalline solid compounds were immediately separated out of the solution on cooling the reaction mixture at room temperature which were filtered in a closed filteration assembly washed with methyl cyanide, dry ether and finally vacuum dried.

Synthesis of tris(pyridine N-oxide) metal (I) chlorosulphates, $[M(PyNO)_3(SO_3Cl)]$ [M = Hg(8), Ag(9)] :

A solution of the metal chlorosulphates (0.04 mole) in boiling methyl cyanide was mixed with an excess (0.12 mole) solution of pyridine N-oxide followed by magnetic stirring which resulted in the isolation of solid products which were vacuum filtered and isolated in the manner described above.

Synthesis of tris(pyridine) metal (I) chlorosulphates, $[M(Py)_3(SO_3Cl)]$ [M = Hg(10), Ag(11)] :

An excess of pyridine (0.06 mole) in boiling methyl cyanide was added to hot metal chlorosulphates (0.02 mole) solution

taken in methyl cyanide. The reaction mixtures were magnetically stirred for 6 hrs. at room temperature affording the isolation of solid mass which were isolated in the manner discussed above.

Synthesis of mono(2,2'-bipyridine) metal (I) chlorosulphates, [M(biPy)(SO_3Cl)] [M = Hg(12), Ag(13)] :

0.02 mole metal chlorosulphate was taken in 20 ml of boiling methyl cyanide in a closed reaction vessel and an excess (0.06 mole) of hot 2,2'-bipyridine solution in methyl cyanide (20 ml) was added. The reaction mixtures were magnetically stirred for 3 hrs. at room temperature resulting in the isolation of solid products. The resultant solid compounds formed were vacuum filtered, washed with dry ether and finally vacuum dried.

Synthesis of mono(acridine) metal (I) chlorosulphates, [M(acr)(SO_3Cl)] [M = Hg(14), Ag(15)] :

0.02 mole metal chlorosulphate was dissolved in boiling methyl cyanide and mixed with an excess (0.06 mole) solution of acridine in boiling methyl cyanide. On cooling the mixture at room temperature, the solid compounds were immediately separated out of the solution which were filtered in a filter-

ation assembly, washed with dry ether and finally vacuum dried.

Synthesis of pyridine, methyl cyanide, acridine, triphenylphosphine and 2,2'bipyridine complexes of metal tris(chlorosulphates) :

These complexes were prepared by mixing stoichiometric amounts of metal tris(chlorosulphates) taken in methyl cyanide with an excess of ligand solution in methyl cyanide. A detailed procedure of the preparation is given as below :

Synthesis of mono(triphenylphosphine) metal(III)chlorosulphates $[M(Ph_3P)(SO_3Cl)_3]$ [M = Cr(16), Mn(17), Fe(18)] :

An excess of triphenylphosphine (0.15 mole) dissolved in methyl cyanide was gradually added to hot metal(III)chlorosulphate solution (0.05 mole) taken in methyl cyanide followed by magnetic stirring at room temperature. The crystalline solid compounds thus formed were vacuum filtered and washed with dry ether and finally dried under vacuum.

Synthesis of tris(pyridine) metal(III) chlorosulphates, $[M(Py)_3(SO_3Cl)_3]$ [M = Cr(19), Mn(20), Fe(21)] :

0.05 Mole of metal tris(chlorosulphate) was reacted with excess of 0.4 mole of hot ligand solution in methyl cyanide in

a closed reaction vessel. The reaction mixtures were magnetically stirred at room temperature resulting in the isolation of solid products which were vacuum filtered, washed with dry ether and vacuum dried.

Synthesis of bis(2,2'-bipyridine) metal(III) chlorosulphates, $[M(bipy)_2(SO_3Cl)_3]$ [M = Cr(22), Mn(23), Fe(24)] :

A solution of the metal tris(chlorosulphate) (0.05 mole) in boiling methyl cyanide was mixed with an excess (0.15 mole) solution of bipyridine in boiling methyl cyanide. The mixture was allowed to cool at room temperature. The crystalline solid compounds thus formed were vacuum filtered and isolated in the manner described above.

Synthesis of tris(acridine) metal(III) chlorosulphates, $[M(acr)_3(SO_3Cl)_3]$ [M = Cr(25), Mn(26), Fe(27)] :

A metal tris(chlorosulphate) (0.05 mole) was dissolved in 20 ml of boiling methyl cyanide in a closed reaction vessel and an excess (0.4 mole) of acridine solution in methyl cyanide (20 ml) was slowly added. The reaction mixture was magnetically stirred for 6 hrs. at room temperature. The crystalline solid compounds thus formed were vacuum filtered and washed with dry ether and finally dried under vacuum.

Synthesis of tris(methyl cyanide) metal(III)chlorosulphates, $[M(MeCN)_3(SO_3Cl)_3]$ [M = Cr(28), Mn(29), Fe(30)] :

The hot concentrated (0.1 mole) solution of metal tris (chlorosulphate) in methyl cyanide (20 ml) was abruptly cooled in closed reaction vessel below room temperature, which resulted in the separation of crystalline solid compound. The content was magnetically stirred for 3 hrs. The products thus formed were isolated in a manner described as above.

The C, H and N analyses were obtained from micro-analytical laboratory of CDRI Lucknow. The analyses for metals Hg, Ag, Cr, Mn, Fe and non metals sulphur and chlorine were determined[81,82] by established methods. The i.r. spectra were recorded as nujol mulls in polyethylene envelopes sealed from all sides using PYE Unicam SP3 - 300 Spectrophotometer. Electrical conductivity was measured for 10^{-3}M solutions, in DMSO or CH_3CN using a systronic bridge model 302 thermostated as 25 ± 0.1°C. The electronic spectra were recorded in DMSO or CH_3CN using a PYE Unicam 8800 Spectrophotometer.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Coordinating Properties of Chlorosulphate ion; Synthesis and Characterization of transition metal mono and tris(chlorosulphates) :

The results of elemental analyses (Table-1) of the compounds (1) and (2) are quite in agreement with the composition as $M(SO_3Cl)$ [M = Hg, Ag]. However, the compounds (3), (4) and (5) corresponds to the composition as $M(SO_3Cl)_3$ [M = Cr, Mn, Fe].

The IR spectra of these compounds (Table-2) exhibit nine medium to strong intensity bands in conformation with the C_s symmetry of covalently bonded chlorosulphate group. The free chlorosulphate group with C_{3v} symmetry has been reported[8] to exhibit six fundamental modes of vibrations[8]. However, as a consequence of covalent bonding of chlorosulphate group, the doubly degenerate E modes split resulting in total nine fundamental modes of vibrations. The splitting of doubly degenerate (E) modes alongwith the positive shift in symmetric SO_3 stretching mode $\nu_1(A)$ may resonably be explained, in terms of lowering of symmetry of SO_3Cl^- group from C_{3v} to a reduced C_s symmetry. The positive shift in $\nu_1(A)$ indicates the existence of a considerable extent of cation-anion interaction resulting in a substantial covalent bonding between the chlorosulphate

Table-1 Yields, Elemental Analyses and Molar Conductivity Values for metal mono and tris(chlorosulphates).

Compounds	Label	Yield (%)	Found (Calcd) (%)			Molar conductance μ_m^*
			Cl	S	M	$Cm^2\ Ohm^{-1}\ Mol^{-1}$
$[Hg(SO_3Cl)]$	(1)	68	10.09 (11.21)	9.85 (10.14)	62.03 (63.45)	62*
$[Ag(SO_3Cl)]$	(2)	70	15.44 (15.87)	15.10 (14.35)	48.45 (48.28)	59*
$[Cr(SO_3Cl)_3]$	(3)	68	25.96 (26.68)	23.99 (24.13)	12.83 (13.04)	47
$[Mn(SO_3Cl)_3]$	(4)	72	27.00 (26.49)	23.16 (23.95)	13.90 (13.68)	40
$[Fe(SO_3Cl)_3]$	(5)	65	26.02 (26.43)	23.04 (23.90)	13.01 (13.87)	45

*in Methyl cyanide

Table - 2 Infra-red Vibrational Frequencies (Cm^{-1}) of metal mono and tris(chlorosulphates) with possible assignments

Compounds	Label	$\nu_6(E)$ S-Cl wag.	$\nu_2(A)$ S-Cl Str.	$\nu_3(A)$ Sym. SO_3 def.	$\nu_5(E)$ Asym. SO_3 def.	$\nu_1(A)$ Sym. SO_3 Str.	$\nu_4(E)$ Asym. SO_3 Str.
$[Hg(SO_3Cl)]$	(1)	310w 330m	425m	560m	630m 650m	1070s	1150s 1190m
$[Ag(SO_3Cl)]$	(2)	315w 320m	400m	580s	620m 670s	1065s	1190m 1260m
$[Cr(SO_3Cl)_3]$	(3)	310w 315m	390m	560s	640m 650s	1080s	1140s 1170m
$[Mn(SO_3Cl)_3]$	(4)	310w 320m	450m	570m	650m 670m	1070s	1160s 1220m
$[Fe(SO_3Cl)_3]$	(5)	310w 320m	455m	570s	650m 680m	1080s	1150m 1220s

w = weak; m = medium; s = strong

ion and the metal ions. This has been further confirmed by the splitting in the doubly degenerate $\nu_4(E)$, $\nu_5(E)$ and $\nu_6(E)$ modes which might be due to the lowering of the symmetry of the chlorosulphate group from C_{3v} symmetry to a reduced C_s symmetry where chlorosulphate group is bonded in a monodentate manner in (1) and (2) compounds or bidentate manner in (3), (4) and (5) compounds.

Electrical conductivities of transition metal mono and tris (chlorosulphates)

The extent to which a compound undergoes dissociation into ions in coordinating solvents depends on factors such as solvent coordinating strength, dielectric constant, the solvation energies of the ions produced and the coordinating strength of the anion towards the metal ion. Methyl cyanide and dimethyl sulphoxide have been found to be a suitable solvent for conductance measurement studies of the electrolytes due to the fact that their dielectric constant are sufficiently large to support ionic dissociation of the compounds. The electrical conductivities of these chlorosulphates have been measured in methyl cyanide and dimethyl sulphoxide in order to assess the extent to which they undergo ionic dissociation in these solvents and to look for possible correlation with anion coordinating strength. The observed molar conductivity values of these

compounds (Table-1) which lie in the 40 - 62 cm^2 $mole^{-1}$ ohm^{-1} range are not only below the typical 2:1 electrolytes which generally have the conductivities in 140 - 220 cm^2 $mole^{-1}$ ohm^{-1} but are also below the range of typical 1:1 electrolytes which are reported[65,72] to be completely ionized in these solvents. The low conductivity of the metal mono and tris (chlorosulphates) might be due to the dipolar nature of the chlorosulphate anion which would favour ion-pair formation in the solution. It may, therefore, possible to suggest that the $[M(MeCN)_3(SO_3Cl)]$ and $[M(DMSO)_3(SO_3Cl)_3]$ may be possible species in the solution. The electrical conductivity data, therefore, support the i.r. spectral findings in that the anion, chlorosulphate group is coordinated to the metal ions.

Magnetic susceptibility measurements and electronic spectroscopic studies of the transition metal tris(chlorosulphates), $M(SO_3Cl)_3$ [M = Cr, Mn, Fe]

The overall geometry of the compounds (3), (4) and (5) have been ascertained after carrying out the magnetic susceptibility measurements and electronic spectral studies. The observed magnetic moment values (Table-3) of $Cr(SO_3Cl)_3$, $Mn(SO_3Cl)_3$ and $Fe(SO_3Cl)_3$ are consistent with the high spin octahedral d^3, d^4 and d^5 systems suggesting the ground states as $^4A_{2g}$, ^5E_g and $^6A_{1g}$, respectively.

The electronic spectra of $Cr(SO_3Cl)_3$ exhibit two bands at 16,250 and 23,470 cm^{-1} assignable to $^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$ transition, respectively indicating octahedral array around the metal ion consistent with that reported[83,84] for Cr^{3+} ion in the electronic spectrum. The electronic spectra of $Mn(SO_3Cl)_3$ exhibits a weak broad band recorded at 20,720 cm^{-1} which may reasonably be assigned to $^5T_{2g} \longleftarrow {}^5E_g$ transition characteristic of the octahedral environment around the metal ion in $Mn(SO_3Cl)_3$[85,86].

However, two bands located in 12,048 - 12,325 cm^{-1} and 18,500 - 19,300 cm^{-1} region have been observed in $Fe(SO_3Cl)_3$ which may, reasonably, be assigned to $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ transition, respectively corresponding to the octahedral geometry around iron (III)[87,88].

Table - 3 Magnetic susceptibility and Electronic spectral values for metal tris(chlorosulphates

Compounds	Label	$\mu_{eff.}$ B.M.	Energies of Band Maxima (cm^{-1})	Assignments
$[Cr(SO_3Cl)_3]$	(3)	3.84	16,250	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			23,470	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			32,300	Charge Transfer
$[Mn(SO_3Cl)_3]$	(4)	4.81	20,720	$^5T_{2g} \longleftarrow {}^5E_g$
$[Fe(SO_3Cl)_3]$	(5)	5.78	12,125	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			19,100	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			22,160	Charge Transfer

<u>The coordinating characteristic of chlorosulphate anion with complex cations - Synthesis and characterization of the complexes of transition metal mono and tris(chlorosulphates)</u> :

The results of elemental analyses (Table 4) of the compounds derived from $M(SO_3Cl)$, (6) - (15) are consistent with composition as $[M(SO_3Cl)L_3]$ [M = Hg, Ag and L = Pyridine, triphenylphosphine, Pyridine N-oxide] and $[M(SO_3Cl)L]$ [L = 2,2'-bipyridine, acridine] whereas complexes derived from $M(SO_3Cl)_3$, (16) to (30) have the compositions as $[M(SO_3Cl)_3L_3]$ [M = Cr, Mn, Fe and L = Pyridine, acridine, methyl cyanide] $[M(SO_3Cl)_3L_2]$ for L = 2,2'-bipyridine and $[M(SO_3Cl)_3L]$ for L = Triphenylphosphine.

The IR spectra of these complexes (Table 5-9) exhibit well resolved absorption bands which may, reasonably be assigned to the coordinated chlorosulphate group as well as those arising from the coordinated ligands. The IR spectra show a positive shift in the position of $\nu_1(A)$ band as compared to that reported for the free SO_3Cl^- group expected to exist in the ionic $CsSO_3Cl$[8]. However, the position of $\nu_1(A)$ band is quite comparable to that observed for the corresponding metal mono(chlorosulphates) and tris(chlorosulphates) indicating the existence of an appreciable cation-anion interaction such that the chlorosulphate group is covalently bonded to the complex cations, $[ML_n]^{m+}$ (L=1,2 or 3, m = 1 or 3). The observed splitting in

Table-4 Yields, Elemental analyses and Molar conductivity values for the complexes of metal mono and tris(chlorosulphates)

Compounds	Label	Yield (%)	Found (Calcd.) (%)						Molar conductance
			Cl	S	M	C	H	N	μ^*_m Ohm^{-1} Cm^2 $Mole^{-1}$
$[Hg(Ph_3P)_3(SO_3Cl)]$	(6)	60	3.01 (3.21)	2.45 (2.90)	19.54 (18.18)	57.09 (58.80)	3.8 (4.11)	-	38
$[Hg(PyNO)_3(SO_3Cl)]$	(8)	65	5.21 (5.89)	4.78 (5.33)	34.12 (33.35)	29.20 (29.95)	2.13 (2.51)	6.14 (6.98)	17
$[Hg(Py)_3(SO_3Cl)]$	(10)	64	5.69 (6.40)	4.92 (5.79)	35.99 (36.24)	31.78 (32.55)	3.40 (2.73)	6.83 (7.59)	33
$[Hg(bp)(SO_3Cl)]$	(12)	70	7.33 (7.50)	5.83 (6.78)	41.99 (42.47)	25.04 (25.43)	2.86 (1.70)	6.64 (5.93)	48
$[Hg(acr)(SO_3Cl)]$	(14)	69	7.00 (7.15)	5.93 (6.47)	41.70 (40.49)	32.40 (31.52)	2.04 (1.83)	2.16 (2.82)	42
$[Ag(Ph_3P)_3(SO_3Cl)]$	(7)	75	3.06 (3.50)	2.86 (3.17)	10.15 (10.67)	65.09 (64.20)	4.02 (4.48)	-	26
$[Ag(PyNO)_3(SO_3Cl)]$	(9)	60	6.06 (6.96)	6.00 (6.30)	20.58 (21.20)	34.64 (35.41)	2.13 (2.97)	9.19 (8.26)	38
$[Ag(Py)_3(SO_3Cl)]$	(11)	64	8.04 (7.69)	6.19 (6.95)	22.68 (23.41)	40.54 (39.10)	3.76 (3.28)	8.68 (9.12)	47
$[Ag(bp)(SO_3Cl)]$	(13)	73	8.99 (9.34)	7.75 (8.44)	28.50 (28.41)	32.31 (31.64)	2.01 (2.12)	6.78 (7.38)	45
$[Ag(acr)(SO_3Cl)]$	(15)	69	9.05 (8.80)	6.88 (7.96)	25.83 (26.79)	37.91 (38.78)	3.11 (2.25)	2.99 (3.47)	43
$[Cr(Ph_3P)(SO_3Cl)_3]$	(16)	72	15.33 (16.09)	13.79 (14.55)	6.68 (7.87)	33.91 (32.71)	3.05 (2.29)	-	46

Contd.....

$[Cr(Py)_3(SO_3Cl)_3]$	(19)	76	16.05 (16.72)	16.41 (15.12)	9.06 (8.17)	27.60 (28.33)	1.65 (2.37)	7.18 (6.61)	38
$[Cr(bp)_2(SO_3Cl)_3]$	(22)	70	14.33 (14.96)	12.76 (13.53)	6.67 (7.31)	32.16 (33.79)	1.86 (2.27)	8.37 (7.88)	37
$[Cr(acr)_3(SO_3Cl)_3]$	(25)	60	10.78 (11.36)	10.91 (10.27)	4.79 (5.55)	49.46 (50.03)	3.46 (2.90)	4.06 (4.49)	35
$[Cr(MeCN)_3(SO_3Cl)_3]$	(28)	66	19.66 (20.38)	19.21 (18.43)	8.75 (9.96)	4.13 (4.60)	0.97 (0.58)	3.10 (2.68)	40
$[Mn(Ph_3P)(SO_3Cl)_3]$	(17)	80	15.87 (16.02)	13.89 (14.49)	7.84 (8.27)	31.68 (32.57)	1.83 (2.78)	-	37
$[Mn(Py)_3(SO_3Cl)_3]$	(20)	78	15.98 (16.65)	14.27 (15.05)	7.28 (8.60)	29.36 (28.20)	1.99 (2.37)	6.93 (6.57)	31
$[Mn(bp)_2(SO_3Cl)_3]$	(23)	81	14.37 (14.90)	12.97 (13.47)	6.74 (7.69)	34.91 (33.65)	3.17 (2.26)	7.06 (7.85)	41
$[Mn(acr)_3(SO_3Cl)_3]$	(26)	65	10.93 (11.32)	9.78 (10.24)	5.26 (5.85)	50.64 (49.88)	3.76 (2.90)	3.83 (4.47)	32
$[Mn(MeCN)_3(SO_3Cl)_3]$	(29)	55	19.75 (20.27)	17.68 (18.33)	11.02 (10.47)	3.97 (4.57)	1.07 (0.58)	2.33 (2.67)	43
$[Fe(Ph_3P)(SO_3Cl)_3]$	(18)	80	17.65 (16.00)	13.36 (14.47)	7.79 (8.40)	32.04 (32.53)	1.97 (2.27)	-	46
$[Fe(Py)_3(SO_3Cl)_3]$	(21)	61	15.33 (16.62)	14.90 (15.03)	9.46 (8.73)	29.46 (28.16)	2.01 (2.36)	7.17 (6.65)	49

Contd.....

$[Fe(bp)_2(SO_3Cl)_3]$	(24)	74	13.96 (14.88)	12.79 (13.46)	6.87 (7.81)	33.01 (33.61)	3.06 (2.26)	8.64 (7.83)	35
$[Fe(acr)_3(SO_3Cl)_3]$	(27)	78	10.79 (11.31)	10.01 (10.23)	6.71 (5.94)	50.60 (49.83)	1.65 (2.89)	3.30 (4.47)	35
$[Fe(MeCN)_3(SO_3Cl)_3]$	(30)	57	19.76 (20.23)	17.93 (18.30)	9.78 (10.62)	3.76 (4.57)	0.29 (0.57)	3.47 (2.66)	39

Ph_3P = Triphenylphosphine; PyNO = Pyridine N-oxide; Py = Pyridine; bp = 2,2'-bipyridine acr = acridine and MeCN = Methyl cyanide.

the doubly degenerate (E) modes further substantiates the above statement suggesting that in these complexes too, the symmetry of SO_3Cl^- group is lowered from C_{3v} to a reduced C_s symmetry.

The IR spectra also exhibit the bands characteristic of the coordinated ligand molecules as discussed below :

The IR spectra of the complexes derived from triphenylphosphine (Table-5) exhibits a strong band at 510 cm^{-1} characteristic of triphenylphosphine and a medium intensity bands in 265 - 270 region which may reasonably be assigned to M-P stretching frequency[68].

The coordination of methyl cyanide molecule in the complexes (Table-6) derived from methyl cyanide has been suggested in view of positive shift in the observed position of $\nu_{C\equiv N}$ stretching frequency ($\sim$35 cm^{-1}) consistent with that reported[36,55,59] for various methyl cyanide complexes where CH_3CN molecule is coordinated via nitrogen of this cyanide group.

It has been reported that ν_{N-O} stretching frequency of Pyridine N-oxide molecule undergoes a considerable negative shift on coordination to divalent metals[36]. It is apparent from (Table-6) that in the present complexes too, the ν_{N-O} band

Table - 5 Infra-red Vibrational Frequencies (cm^{-1}) of the complexes of metal mono and tris(chlorosulphates) with triphenylphosphine

Compounds	Label	$\nu_6(E)$	$\nu_2(A)$	$\nu_3(A)$	$\nu_5(E)$	$\nu_1(A)$	$\nu_4(E)$	PPh_3
$[Hg(Ph_3P)_3(SO_3Cl)]$	(6)	310m 320w	450m	560m	610m 625m	1070s	1150s 1210m	1470s, 1100s, 740s, 510s, 265m
$[Ag(Ph_3P)_3(SO_3Cl)]$	(7)	320m 350m	460m	570m	620s 650m	1070s	1165m 1240m	1450s, 1100m, 740m, 500s, 275m
$[Cr(Ph_3P)(SO_3Cl)_3]$	(16)	320m 340s	425s	570m	590s 610m	1080s	1210m 1260m	1430s, 1095s, 740s, 500s, 270m
$[Mn(Ph_3P)(SO_3Cl)_3]$	(17)	315w	460m	580s	660s 690m	1070s	1190s 1245m	1450s, 1095s, 745s, 510s, 275m
$[Fe(Ph_3P)(SO_3Cl)_3]$	(18)	330w 370s	450m	560m	640m 680m	1070s	1170s 1230m	1480s, 1100s, 740s, 510s, 270m

m = medium, w = weak, s = strong

Table - 6 Infra-red Vibrational Frequencies (cm^{-1}) of the complexes of metal mono and tris(chlorosulphates) with Pyridine N-oxide and methyl cyanide

Compounds	Label	$\nu_6(E)$	$\nu_2(A)$	$\nu_3(A)$	$\nu_5(E)$	$\nu_1(A)$	$\nu_4(E)$	ν_{M-O}	ν_{N-O}	$\nu_{C\equiv N}$	$\Delta\nu_{C\equiv N}$
$[Hg(PyNO)_3(SO_3Cl)]$	(8)	320m 360w	445m	580s	630m 650m	1065m	1180s 1210m	385m	1220s	-	-
$[Ag(PyNO)_3(SO_3Cl)]$	(9)	330w 350m	445m	585s	635m 660m	1070m	1160m 1260s	375m	1225s	-	-
$[Cr(MeCN)_3(SO_3Cl)_3]$	(28)	330w	460m	575s	630m 660m	1080s	1185m 1240s	-	-	2285s	30
$[Mn(MeCN)_3(SO_3Cl)_3]$	(29)	320m	455m	580s	620m 690m	1065s	1180m 1230s	-	-	2290s	35
$[Fe(MeCN)_3(SO_3Cl)_3]$	(30)	325m	440m	580s	650s 670m	1080s	1190m 1230s	-	-	2275s	20

w = weak, m = medium, s = strong

undergoes negative shift of about 25 cm^{-1}, compared to that reported[69-70] for free pyridine N-oxide (1243 cm^{-1}) suggesting the coordination of pyridine N-oxide to metal ions. A band of medium intensity observed in 375 - 385 cm^{-1} may reasonably be assigned for ν_{M-O}.

It has been observed that the free pyridine molecule exhibit three important ring vibrations viz. 6a and 8a (in-plane ring deformation) appearing as 601 and 1578 cm^{-1}, respectively[62] and 16b (out-of plane ring deformation) appearing at 403 cm^{-1} undergo positive shift (Table-7) suggesting its coordination to the metal ions[36].

However, the doubling of the 8a mode may be due either to inter or intramolecular interactions of the pyridine molecule in the crystal lattice[89].

The complexes derived with 2,2'-bipyridine (Table-8) also exhibit three characteristic ring vibrations i.e. 16b (out-of plane ring deformation), 6a and 8b (in-plane ring deformation) appearing at 402, 619 and 1590 cm^{-1}, respectively[63]. The two lower wave number bands which have been reported to be very sensitive and thus undergo a positive shift on coordination, similar to that reported earlier[36,38].

In case of acridine complexes (Table-9) the coordination to metal ions through the nitrogen has been inferred from the

Table - 7 Infra-red Vibrational Frequencies (cm^{-1}) of the Complexes of metal mono and tris(chlorosulphates) with Pyridine

Compounds	Label	$\nu_6(E)$	$\nu_2(A)$	$\nu_3(A)$	$\nu_5(E)$	$\nu_1(A)$	$\nu_4(E)$	16b	6a	8a
$[Hg(Py)_3(SO_3Cl)]$	(10)	330m	440m	580m	620s 635s	1070s	1180s 1230m	430m	620s	1590s 1630s
$[Ag(Py)_3(SO_3Cl)]$	(11)	325w	450m	560s	620s 670m	1080s	1150s 1260m	425s	620s	1580s 1620s
$[Cr(Py)_3(SO_3Cl)_3]$	(12)	330m 340s	450m	575m	625s 690m	1070s	1160s 1230m	420s	645m	1590s 1640s
$[Mn(Py)_3(SO_3Cl)_3]$	(20)	330m 350m	445m	560s	640s 670m	1085vs	1190s 1265s	430m	630s	1575s 1620s
$[Fe(Py)_3(SO_3Cl)_3]$	(21)	320w 350m	460m	565s	610s 640s	1085vs	1185s 1230m	420m	625s	1620s 1630s

w = weak, m = medium, s = strong, vs = very strong

Table-8 Infra-red Vibrational Frequencies (cm^{-1}) of the Complexes of metal mono and tris(chlorosulphates) with 2,2'-bipyridine.

Compounds	Label	$\nu_6(E)$	$\nu_2(A)$	$\nu_3(A)$	$\nu_5(E)$	$\nu_1(A)$	$\nu_4(E)$	16b	6a	8a
$[Hg(bp)(SO_3Cl)]$	(12)	320m 370w	450m	570s	620m 640m	1070s	1160s 1230m	420m	660s	1590s 1630s
$[Ag(bp)(SO_3Cl)]$	(13)	330m 350w	435m	580s	630m 670s	1080s	1180s 1270m	425s	665s	1595s 1685m
$[Cr(bp)_2(SO_3Cl)_3]$	(22)	325m 355m	440m	570s	620m 650s	1075s	1190s 1230s	420m	650s	1605s 1635m
$[Mn(bp)_2(SO_3Cl)_3]$	(23)	325m 340s	430m	575m	665m 690s	1075s	1180s 1240m	430m	655s	1620s 1660s
$[Fe(bp)_2(SO_3Cl)_3]$	(24)	310m	430m	580s	620m 670s	1080s	1175s 1220m	430m	660s	1610s 1640m

m = medium, s = strong

Table - 9 Infra-red Vibrational Frequencies (cm^{-1}) of the complexes of metal mono and tris(chlorosulphates) with Acridine.

Compounds	Label	$\nu_6(E)$	$\nu_2(A)$	$\nu_3(A)$	$\nu_5(E)$	$\nu_1(A)$	$\nu_4(E)$	$\nu_{C=C}$ $\nu_{C=N}$
$[Hg(acr)(SO_3Cl)]$	(14)	310w 330m	460s	580s	660m 680s	1080s	1170s 1215m	1580s 1605m 1620sh
$[Ag(acr)(SO_3Cl)]$	(15)	300m 320m	440s	565s	640s 670s	1085s	1190m 1240s	1570s 1620sh 1630m
$[Cr(acr)_3(SO_3Cl)_3]$	(25)	320m 330m	465s	580s	620s 650m	1090s	1175s 1230s	1575s 1600s 1625m
$[Mn(acr)_3(SO_3Cl)_3]$	(26)	310w 325m	450s	560s	610s 630m	1075m	1160s 1225s	1590m 1620sh 1640s
$[Fe(acr)_3(SO_3Cl)_3]$	(27)	320m	470s	565s	650s 680m	1070m	1170s 1220m	1585m 1610sh 1630s

m = medium, w = weak, s = strong, sh = shoulder

positive shift in the C=C and C=N stretching vibrations[64,65]. The observed position of the bands corresponding to C=C and C=N have been found to be in conformation with the earlier reports[36,38].

The confirmation regarding the covalent bonding of chloro sulphate group have been further corroborated by observed low electrical conductivity values of these complexes in dimethyl sulphoxide.

The geometry of the complexes (16) to (30) is identical to that of the corresponding metal tris(chlorosulphates) as is indicated from the results of the magnetic susceptibility and ligand field spectroscopic studies.

The observed magnetic moments (Table-10) for all the chromium complexes are nearly the same as expected for spin free octahedral d^3 system suggesting the expected ground state as $^4A_{2g}$. This has been further confirmed by observed positions of the absorption bands in the electronic spectra which appear in the range 15,840 - 16,340 cm^{-1} and 22,945 - 23,900 cm^{-1} assignable to $^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \longleftarrow {}^4A_{2g}$ transition, respectively consistent with the octahedral geometry around chromium(III) ion[83,84].

The magnitude of magnetic moments for the complexes of Mn(III) (Table-11) are quite consistents with the expected

Table - 10 Magnetic Susceptibility and Electronic Spectral Values for the Complexes of Chromium tris(chlorosulphate)

Compounds	Label	$\mu_{eff.}$ B.M.	Energies of Band Maxima (cm^{-1})	Assignments
$[Cr(Ph_3P)(SO_3Cl)_3]$	(16)	3.88	16,340	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			23,530	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			33,310	Charge transfer
$[Cr(Py)_3(SO_3Cl)_3]$	(19)	3.85	16,030	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			23,900	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			31,420	Charge transfer
$[Cr(bp)_2(SO_3Cl)_3]$	(22)	3.83	15,840	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			22,945	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			32,845	Charge transfer
$[Cr(acr)_3(SO_3Cl)_3]$	(25)	3.87	15,965	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			23,445	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			33,040	Charge transfer
$[Cr(MeCN)_3(SO_3Cl)_3]$	(28)	3.89	16,075	$^4T_{2g}(F) \longleftarrow {}^4A_{2g}(F)$
			23,400	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}(F)$
			33,900	Charge transfer

octahedral environment around the metal ions. The electronic spectra exhibit a weak broad band in 20,600 - 20,950 cm^{-1} region which may, reasonably, be assigned to $^5T_{2g} \longleftarrow {}^5E_g$ transition characteristic of the octahedral environment around the metal ion[85,86].

However, the observed magnetic moments and the ligand field spectra of all the complexes of iron(III) (Table-12) are similar to that observed for the iron tris(chlorosulphates) suggesting an octahedral array of ligands around the metal ion. The spectra consist of a band in the range 12,060 - 12,850 cm^{-1} and 18,620 - 19,310 cm^{-1} characteristic of $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ transition, respectively[87,88].

Table-11 Magnetic Susceptibility and Electronic Spectral Values for the complexes of manganese tris(chlorosulphate)

Compounds	Label	$\mu_{eff.}$ B.M.	Energies of Band Maxima (cm^{-1})	Assignments
$[Mn(Ph_3P)(SO_3Cl)_3]$	(17)	4.79	20,600	$^5T_{2g} \longleftarrow {}^5E_g$
$[Mn(Py)_3(SO_3Cl)_3]$	(20)	4.86	20,890	$^5T_{2g} \longleftarrow {}^5E_g$
$[Mn(bp)_2(SO_3Cl)_3]$	(23)	4.80	20.950	$^5T_{2g} \longleftarrow {}^5E_g$
$[Mn(acr)_3(SO_3Cl)_3]$	(26)	4.89	20,810	$^5T_{2g} \longleftarrow {}^5E_g$
$[Mn(MeCN)_3(SO_3Cl)_3]$	(29)	4.85	20,865	$^5T_{2g} \longleftarrow {}^5E_g$

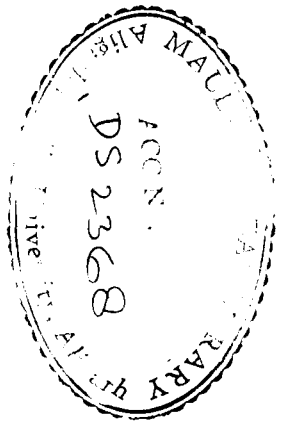


Table - 12 Magnetic Susceptibility and Electronic Spectral Values for the Complexes of Iron tris(chlorosulphate)

Compounds	Label	$\mu_{eff.}$ B.M.	Energies of Band Maxima (cm^{-1})	Assignments
$[Fe(Ph_3P)(SO_3Cl)_3]$	(18)	5.75	12,235	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			18,700	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			24,140	Charge transfer
$[Fe(Py)_3(SO_3Cl)_3]$	(21)	5.80	12,060	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			19,165	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			22,435	Charge transfer
$[Fe(bp)_2(SO_3Cl)_3]$	(24)	5.83	12,600	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			19,310	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			22,065	Charge transfer
$[Fe(acr)_3(SO_3Cl)_3]$	(27)	5.79	12,850	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			18,620	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			22,100	Charge transfer
$[Fe(MeCN)_3(SO_3Cl)_3]$	(30)	5.82	12,600	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
			19,260	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
			23,510	Charge transfer

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